Microporous and Mesoporous Materials 267 (2018) 93–99

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Facile synthesis of mesoporous 3D CoO/nitrogen-doped graphene aerogel as high-performance anode materials for lithium storage

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ARTICLE INFO

Keywords:
CoO
Mesoporous
Nitrogen doping
Graphene aerogel
Anode materials
Lithium ion batteries

ABSTRACT

CoO has been considered as a novel anode material for lithium storage due to its high theoretical capacity. Herein, mesoporous 3D CoO/nitrogen-doped graphene aerogel (CoO/NGA) is constructed by a facile solvothermal approach followed by subsequent annealing. The NGA is prepared by using dimethylmethanamide (DMF) as a reducing agent and nitrogen source. Ultrafine CoO nanocrystals are homogeneously distributed and tightly anchored on the 3D macroscopic NGA frameworks. The 3D NGA can not only effectively restrain the agglomeration of CoO nanocrystal but also accelerate ion and electron transport through 3D networks. Benefiting from the combine of the two characteristics, the unique CoO/NGA anode exhibits an outstanding cycling stability, showing a specific capacity of 896 mAh g^{-1} at 200 mA g^{-1} after 200 cycles.

1. Introduction

Lithium ion batteries (LIBs) have been extensively utilized in hybrid electric vehicles (HEVs) and electric vehicles (EVs) on account of their several important advantages, such as high energy density, no memory effect, long cycle life, and low self-discharging [1,2]. Transition metal oxides (TMOs)/carbon composites have achieved intensive attention as one of the prospective material for application in LIBs [3,4]. Graphene has been a leading candidate for various electrochemically active TMOs with superior performance due to its high electronic conductivity, large surface area, chemical and thermal stability, as reported by extensive studies [5–10]. Most of previous works were concentrated on preparation of two-dimensional (2D) graphene-based composites in which nanoparticles anchored onto the surface of graphene sheets (GS). In most cases, the 2D GS would easily restack and re-aggregate during drying due to the van der Waals forces, significantly reducing the accessible surface area and limiting electron/ion transport. Furthermore, GS usually possess a limited number of reactive sites, resulting to a low specific capacity, large irreversible capacity, and fast capacity fading. Therefore, it is still a big challenge to further optimize their electrochemical performance [11–13].

To overcome these issues, it is believed that two strategies are feasible. The first one is to assemble 2D GS into macroscopic 3D GA. Shi [14] and Wang [15] first reported a facile hydrothermal treatment to prepare 3D graphene. The 3D structure can effectively prevent restacking of graphene and provide graphene-based composites with large specific surface area, more active sites, and fast electron transport kinetics. Therefore, many 3D TMOs/GA composites have been reported such as Fe_2O_3/GA [16], Fe_3O_4/GA [17], CoO/GA [18], Co_3O_4/GA [19], and SnO_2/GA [20,21] to prepare by the hydrothermal treatment. Normally, reducing agents such as $NaHSO_3$, $SnCl_2$, $FeSO_4$ are used to prepare SnS/GA [22], SnO_2/GA [23], and Fe_3O_4/GA [24] under mild conditions (oil bath at 95 °C). All the works above demonstrate the effective macroscopic 3D architectures to enhance the lithium storage properties. Apart from the geometrical control, nitrogen doping of GS is another effective way to improve lithium storage performance by modulating the electronic structure of graphene, creating defects to decrease the energy barrier of lithium penetration, and enhancing reactive sites [25].

Some works have been done to combine the two characteristics together. $NH_3{\cdot}H_2O$, polypyrrole, and urea were reported as nitrogen sources to prepare Fe_2O_3/NGA [26] and Fe_3O_4/NGA [27–29]. For the former, the toxicity of the nitrogen source should be considered, and the later often requires rigorous conditions or special instruments. Therefore, it is still a challenge to prepare TMOs/NGA by a facile method. Recently, a solvothermal method in N,N-dimethylmethanamide (DMF) were reported to be an effective way to solve above problems [30,31]. To the best of our knowledge, there are few reports

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https://doi.org/10.1016/j.micromeso.2018.03.025
Received 20 January 2018; Received in revised form 6 March 2018; Accepted 20 March 2018

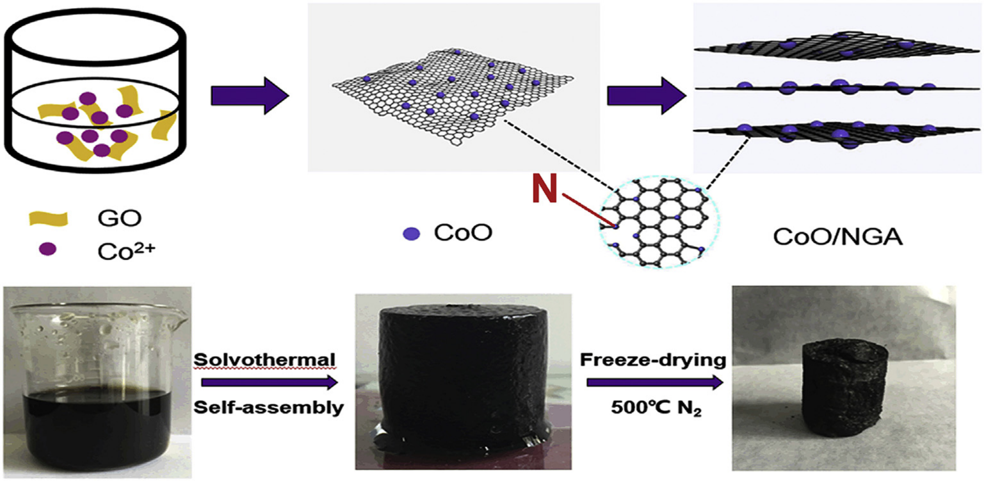

Fig. 1. Scheme of the experimental procedure of CoO/NGA composites.

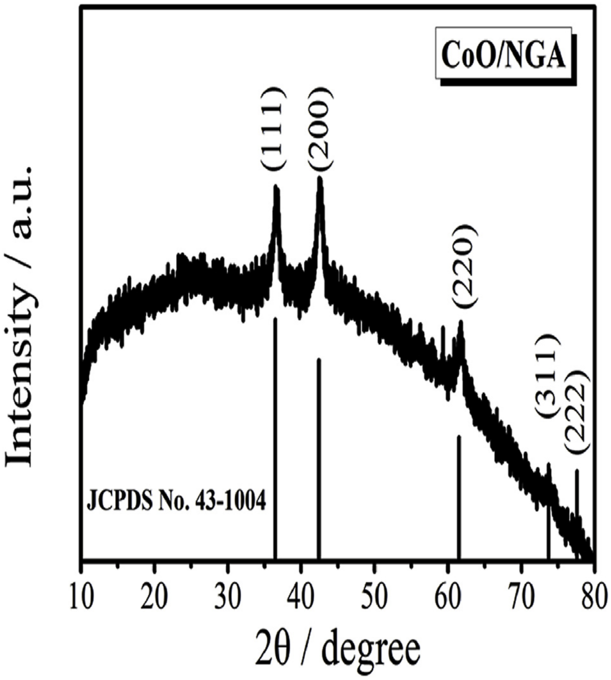

Fig. 2. XRD patterns of CoO/NGA composites.

about CoO/NGA materials used in lithium ion batteries. Here we report a novel solvothermal-induced self-assembly approach to construct 3D CoO/NGA as anode materials for LIBs. It was discovered that CoO dispersed onto the unique 3D NGA can combine the merits of macroscopic 3D architectures and nitrogen-doping properties. The as-prepared composites exhibit excellent capability stability and good rate performance.

2. Experimental section

2.1. Materials synthesis

Graphene oxide (GO) was synthesized from graphite powder by the modified hummers' method. The aqueous GO dispersion were freeze-dried and the GO powder was collected for further use. In a typical synthesis process, 100 mg of the as-prepared GO powder were dissolved into 50 mL DMF solvent, followed by ultra-sonicated for 2 h to get the GO dispersion in DMF. Then, 2 mmol cobalt acetate was added. The mixed suspension were transferred into a 100 mL Teflon container sealed in steel autoclave, and reacted under 180 °C for 12 h. The obtained monolith was washed repeatedly with distilled water, freeze-dried, and calcined at 500 °C for 2 h at 5 °C min^{-1} in N_2 atmosphere to obtain CoO/NGA. As comparison, pure CoO and NGA were synthesized by similar method without adding GO and cobalt acetate.

2.2. Characterization

Field emission scanning electron microscopy (FESEM, JSM-7001F) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-3010) were used to perform the morphology experiments of CoO/NGA. The crystalline structure was characterized by X-ray diffraction (XRD) measurements on Rigaku D/max-2500 with Cu Kα radiation ($\lambda = 1.54056$ Å). The thermal gravimetric analysis (TGA) was determined in air with the temperature ramp of 10 °C min^{-1} from 40 to 800 °C. The Brunauer-Emmet-Teller (BET) curves of the samples were tested by a Micromeritics Model ASAP 2460. The composition of the samples was analyzed with an ESCALAB 250 X-ray photoelectron spectrometers (XPS). Raman spectra was conducted on JY HR800.

2.3. Electrode preparation and electrochemical measurements

For electrode preparation, the mixture of active materials (80 wt%), acetylene black (10 wt%), and poly (vinylidene fluoride) (10 wt%) were transferred onto a copper foil and dried at 120 °C for 12 h in a vacuum oven. Then coin cells were assembled in an argon-filled glove box (Mikrouna, H_2O, $O_2 < 0.1$ ppm) using the as-prepared electrode as working electrode, lithium foil as counter electrode and 1 M $LiPF_6$ in a 1: 1 (v/v) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) as the electrolyte. Cyclic voltammetry (CV, 0.1 mV s^{-1}, 0.01–3.00 V vs. Li^+/Li) and electrochemical impedance spectra (EIS, 5 mV amplitude, 100 kHz-0.01 Hz) were conducted by CS310 electrochemical workstation. The discharge-charge profiles were measured with various current densities using a Land battery CT 2001A battery test system (Wuhan, China) in the voltage range of 0.01–3.00 V (vs. Li^+/Li).

3. Results and discussion

As illustrated in Fig. 1, the 3D macroscopic CoO/NGA was fabricated by two steps. The first step was a solvothermal self-assembly strategy. During the process, the Co^{2+} cations were positively charged, while GO was negatively charged ascribed to the presence of oxygen-containing functional groups. Driven by strong electrostatic attractive interaction, Co^{2+} cations can favorably bind on the surface of GO when they mixed together. Subsequently, solvothermal treatment in DMF